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13. ABSTRACT *(Maximum 200 words)*

Work on a number of boron hydride anions and cations has been carried out using the unique features of flowing afterglow-selected ion flow tube (FA-SIFT) technology. Reaction of strong base with diborane has allowed the preparation of a number of anionic boron hydride clusters. Many of these including B_2H_3- have been examined in terms of their reaction chemistry (FA-SIFT) and structure (*ab initio computation*). The fundamental thermodynamic property of gas phase acidity has been measured for several boron hydride species by reacting their corresponding conjugate base with a series of reference acids. Nevertheless, the boron hydride anions have proved to be surprisingly unreactive, particularly considering their low-valency. As a result, studies on simple boron hydride cations like BH_2^+ were undertaken. This cation is particularly specific in its reactions with D_2 and CH_4 in contrast to its periodic neighbor CH_3^+. It reacts with D_2 to give predominantly BHD^+ and HD. The reaction potential surface for this and related reactions has been studied by *ab initio* methods. Electron structure computations have also been carried out in collaboration with Professor M. S. Gordon on various titanium and silicon hydride species.

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COMPLETED PROJECT SUMMARY

TITLE: GAS PHASE STUDIES OF BORON, SILICON, AND
                        ALUMINUM-- RELATIONSHIP TO CARBON-
                        CARBON COMPOSITIES

INCLUSIVE DATES: 3/15/92 TO 5/14/95

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PUBLICATIONS: "Gas-Phase Ion Chemistry of Boron Hydride Anions"
                        M. Krempp, R. Damrauer, C. H. DePuy, Y. Keheyan,
                        J. Am. Chem. Soc.116, 3629 (1994)

                        "Ab Initio Study of Cyclic Siloxanes" T. Kudo, F.
                        Hashimoto, M. S. Gordon, in second draft, to be
                        submitted to either J. Comp. Chem. or Main Group
                        Chemistry

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS: The major
objectives of this research were to use gas phase ion techniques to study ions of
Groups 4, 13, and 14 that might have a realtionship to oxidative processes that
limit the performance of high-temperature carbon-carbon composites. These
powerful gas phase techniques had been generally applied to small systems. Our
proposed work was to examine the possibility of dealing with far larger and less
volatile systems. We have show that larger systems could be made and studied
(eg. the boron hydride and carborane anion clusters), but that their reactivity was
far less than anticipated. Study of their chemistry was limited by reactivity and
difficulties of identifying unequivocally the structure of mass selected anions
having more than two boron atoms. Certain reactivity patterns were established,
but, in general, this aspect of the work was time-consuming and dissappointing.
We determined that study of Group 4 anions might suffer the same fate and
decided to approach their study by computational methods. This work was
undertaken in collaboration with Professor M. S. Gordon (Group 14 collaboration
as well). Our experimental work shifted to the study of small cations in an attmept
to discover more reactive species. The reactivity of the BH_2^+ and related boron

cations proved a rich area for study. Remarkably specific reactions with D_2 and CH_4 contrasted markedly with the chemistry of cations of carbon. Thus, BH_2^+ reacts with D_2 to give BHD^+ and HD overwhelmingly, while CH_3^+ gives virtually complete scrambling. Ab initio investigation of the potential energy surfaces of such reactions have been undertaken and give a consistent picture of reactivity. Interruption of funding of this project made it impossible to meet its full objectives, but some progress in understanding the reactivity of various anions and cations of boron was made.

Final Report
Grant Number F49620-92-J-0182

Introduction: This is the final report for grant number **F49620-92-J-0182** . It summaraizes our work carried out between 4/14/93 and 5/15/95. We have undertaken a broad study of the anion and cation chemistry of boron hydrides and carboranes using selected ion flow tube (SIFT) techniques in a flowing afterglow apparatus. We have prepared a number of unusual ions using these techniques, spending considerable effort characterizing them by both chemical and computational means.. We have also have undertaken collaborative *ab initio* computational studies with Professor Mark S. Gordon to explore the chemistry of various titanium-containing species that proved impractical to study by flowing afterglow methods.

Brief Description of Flowing Afterglow Instrument: All experiments were carried out at room temperature in a tandem flowing afterglow-selected ion flow tube (FA-SIFT) (see schematic diagram), which consists of four sections: a source (first) flow tube for ion preparation, an ion separation and
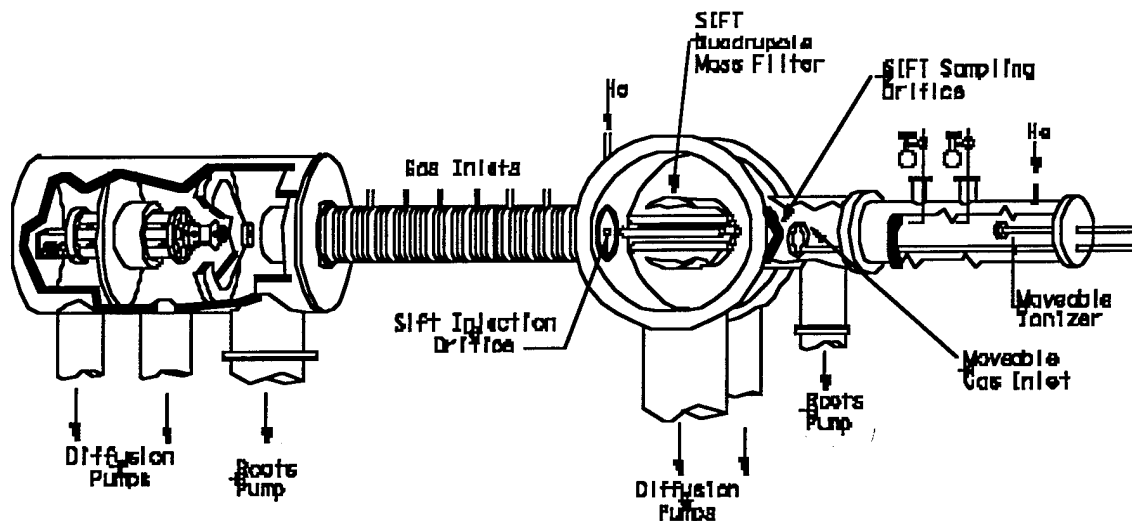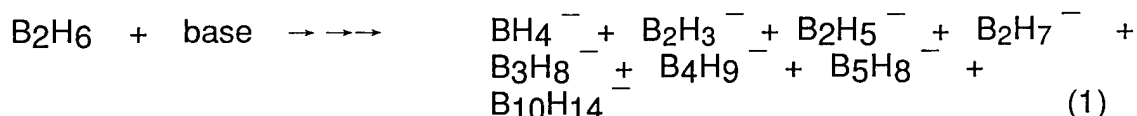

purification region, a second flow tube for studying the chemical reactions of the selected ions, and an ion detection region. In a typical experiment to generate negative ions, hydroxide ions are generated in the first flow tube and are entrained in a rapidly flowing helium stream (0.4 torr). Various neutral species are added downstream through a moveable inlet where rapid reaction ensues producing a variety of ionic products. At the end of the first flow tube these ions are sampled through an orifice into the ion separation region. The helium and other neutrals are removed by pumping while the ions are focused into a quadrupole mass filter by a series of electrostatic lenses. This SIFT quadrupole can be tuned to an appropriate m/z and the desired ion can be injected into the second flow tube, where it is entrained in helium (0.5 torr). The reaction chemistry of the injected ion can then be probed by the addition of a variety of neutral reactants. At the end of the second flow tube, the ionic products are

sampled through an orifice, mass analyzed, and detected by an electron multiplier. It is important to recognize that neutral products are not detected, but are assumed based on mechanistic rationale. Positve ions have been generated by electron impact on diborane followed by mass selection as described above.

To inject ions from the low pressure (10^{-6} torr) region of the SIFT quadrupole into the higher pressure region of the second flow tube, they must be extracted by an electrical potential which imparts kinetic energy to them. Multiple collisions with the helium buffer gas generally cool such ions; however, if the potential is made sufficiently high, ions can often undergo collision-induced dissociation (CID) forming new ions. In a field-free region, the resulting ions can subsequently undergo multiple collisions with helium where they are usually cooled to room temperature before being allowed to react with neutral reagents. The injection potential leading to decomposition of ions is the potential difference between the ion source and the injector plate. The resulting exact kinetic energy of the ions is a sensitive function of a variety of factors, but is not well characterized in our current instrument.

Anion Studies of Diborane: Diborane was the most extensively studied boron compound during this project, both in terms of negative and positive ion studies. It undergoes reaction with anions like F^-, O^-/O_2^-, and HS^- as well as several boron-containing anions; however, its reactivity in the presence of strong bases, particularly HO^- and H_2N^-, has been the major focus of our studies. Generally, the boron-containing anions that have been studied in this project are far less reactive than we had anticipated, undoubtedly because of their characteristic electron deficiency. Equation 1 summarizes the reaction of diborane with strong base:

$$B_2H_6 + base \rightarrow \rightarrow \rightarrow \quad BH_4^- + B_2H_3^- + B_2H_5^- + B_2H_7^- + B_3H_8^- + B_4H_9^- + B_5H_8^- + B_{10}H_{14}^- \quad (1)$$

The most remarkable aspect of equation 1 is the formation of a variety of boron hydride clusters. These cluster anions presumably could form either by proton abstraction from a series of boron hydrides or by anion-molecule reactions of diborane. Interestingly, electron impact of diborane in the flowing afterglow source yields only traces of boron hydride clusters in sharp contrast with studies carried out by Dunbar in the late 1960's using ion cyclotron resonance technology.
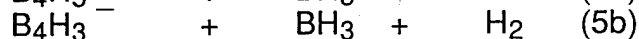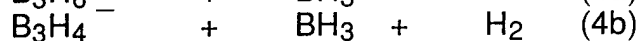
Our current flowing afterglow instruments possess remarkable flexibility for mass selection and collision-induced dissociation (CID), thus making a complicated reaction mixture amenable to further study. Consequently, we have selected several anions for further study. In favorable circumstances, we can carry out CID of ions to generate ions not formed in the source. This technique has been important in the study of various anions. A major drawback of the work to be described subsequently results because the boron-containing compounds we have studied contain naturally abundant boron (one exception-- *vide infra*). Thus, anions with large numbers of boron atoms (when detected mass spectrometrically in the flowing afterglow) possess broad isotopic mass distributions that sometimes overlap, making mass selection occasionally

uncertain. These studies have typically used naturally occurring compounds to chart the most fruitful areas for study.

We have mass selected $B_2H_5^-$, $B_3H_8^-$, $B_4H_9^-$, $B_5H_8^-$, and $B_{10}H_{14}^-$ from the diborane/ base reaction mixture for further study. In each case, CID studies of the anions revealed typical dissociation patterns for collision with helium. In addition, the reaction chemistry of several of these anions and their CID products with various characterization reagents have been undertaken.

To explore the possibility that the boron hydride cluster anions might form by simple anion-molecule reactions of diborane, we have examined diborane's reactivity with boron-containing anions. Reaction of mass selected $^{11}BH_4^-$ with B_2H_6 gives several anions: $^{10}BH_4^-$, $B_2H_7^-$ (trace), and $B_3H_{10}^-$ (trace). No larger clusters were observed, however. Mass selected $B_3H_8^-$, which forms from $B_2H_5^-$ and B_2H_6, did not react with diborane. We conclude from these experiments that the higher cluster anions were likely formed by pyrolysis reactions occurring on the filament of the source rather than anion-molecule reactions from smaller boron hydride anions and diborane.

Collision-Induced Dissociation of Boron-Containing Anions: The most surprising aspect of our work involves the observation of a wide variety of boron-containing anions of quite unusual composition. Anions with high boron-to-hydrogen ratios are routinely observed. The CID's of several mass selected anions are given in the following equations:
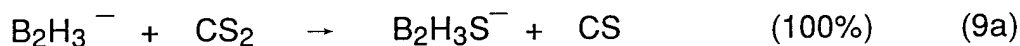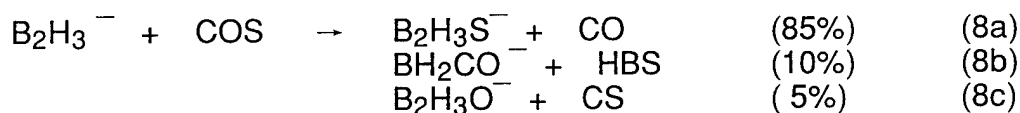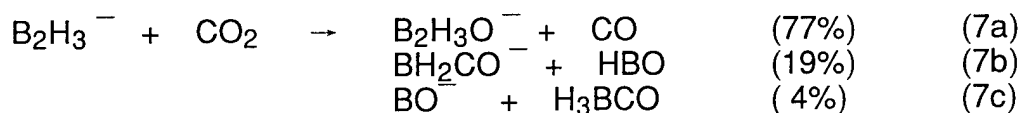
$$B_2H_5^- \rightarrow B_2H_3^- + H_2 \tag{2}$$

$$B_3H_8^- \rightarrow B_2H_5^- + BH_3 \tag{3}$$

$$B_4H_9^- \rightarrow \begin{array}{llll} B_3H_6^- & + & BH_3 & \tag{4a} \\ B_3H_4^- & + & BH_3 + H_2 & \tag{4b} \\ B_2H_3^- & + & 2BH_3 & \tag{4c} \end{array}$$

$$B_5H_8^- \rightarrow \begin{array}{llll} B_4H_5^- & + & BH_3 & \tag{5a} \\ B_4H_3^- & + & BH_3 + H_2 & \tag{5b} \\ B_3H_2^- & + & 2BH_3 & \tag{5c} \end{array}$$

$$B_{10}H_{14}^- \rightarrow \begin{array}{lll} B_{10}H_{13}^- & + & B_{10}H_{12}^- & + \tag{6} \\ B_{10}H_{11}^- & + & B_{10}H_9^- & + \\ B_9H_{11}^- & + & B_9H_9^- & + \\ B_8H_8^- & + & B_8H_6^- & + \\ B_7H_5^- \end{array}$$

Specific studies of some of these anions are outlined below and in an earlier progress report.

The $B_2H_3^-$ Anion: Conditions in the source region of the flowing afterglow can be adjusted so that $B_2H_3^-$ can be mass selected for further study. To do so requires that higher cluster formation be minimized, since $B_2H_3^-$ arises from $B_2H_5^-$ (eq. 2). Some of this work has been published recently (see J. Am. Chem. Soc. **1994** *116*, 3629).

$B_2H_3^-$ is the conjugate base of B_2H_4, a boron hydride that has been studied computationally in detail. Only one experimental study has been reported. The most recent computational study suggests that two isomers of B_2H_4, a doubly H-bridged (C_{2v}) and a perpendicular structure (D_{2d}), are nearly identical in energy and likely interconvert by a low energy pathway that preserves C_2 symmetry.

We have studied $B_2H_3^-$ in detail, measuring the ΔG^o_{acid} of its conjugate acid, B_2H_4 (sometimes called diborane [4]), to be 352.5 ± 5 kcal/mol by bracketing techniques (this is the free energy of the process $HA \rightarrow H^+ + A^-$; thus, the greater the magnitude of this quantity, the weaker the acid). We have also studied its reaction chemistry in detail. A summary of some of our results is given in the referenced paper. Typically, we study mass selected $^{10}B^{11}BH_3^-$, since this isotope distribution removes any mass selection ambiguities and makes product identification easier. The reagents that we typically use for the characterization of anions, namely CO_2, COS, CS_2, all react with $B_2H_3^-$, giving $B_2H_3X^-$ (with X = O for CO_2, and X = S for COS and CS_2) as their major product (eqs. 7-9).

$$B_2H_3^- + CO_2 \rightarrow \quad B_2H_3O^- + CO \quad (77\%) \quad (7a)$$
$$BH_2CO^- + HBO \quad (19\%) \quad (7b)$$
$$BO^- + H_3BCO \quad (4\%) \quad (7c)$$

$$B_2H_3^- + COS \rightarrow \quad B_2H_3S^- + CO \quad (85\%) \quad (8a)$$
$$BH_2CO^- + HBS \quad (10\%) \quad (8b)$$
$$B_2H_3O^- + CS \quad (5\%) \quad (8c)$$

$$B_2H_3^- + CS_2 \rightarrow \quad B_2H_3S^- + CS \quad (100\%) \quad (9a)$$

The result for COS, where the CO-to-CS ratio is 17, suggests that the loss of the more stable CO is the driving force for reaction. The next most prevalent product in the reactions with CO_2 and COS, BH_2CO^-, suggests a common intermediate for both the a and b reaction channels. The reactions of this anion and SO_2 and O_2 have also been studied (and have been tabulated in a previous report). In contrast with the reactions of CO_2, COS, and CS_2, which have efficiencies between 12 and 40%, the reaction with SO_2 occurs at virtually every collision (87% efficiency) while reaction with O_2 is very inefficient (0.5%). These are quite complex reactions, which are typical of other reactions of these neutral species.

The $B_2H_5^-$ Anion: This anion, the conjugate base of diborane, has been studied in less detail. A preliminary survey of its reaction chemistry indicates quite attenuated reactivity in comparision with $B_2H_3^-$. For example, it does not react with CO_2 or O_2 and reacts only slowly with CS_2. We have determined the ΔG^o_{acid} of diborane [6] to be 354 ± 5 kcal/mol. Thus, B_2H_6 and B_2H_4 have nearly identical acidities.

The B$_5$H$_8^-$ Anion: This anion has a well characterized *nido* structure with its five boron atoms in a square pyramidal arrangement. Each boron has a B-H bond; in addition, there are three bridging H's. We have determined the ΔG^o_{acid} of B$_5$H$_9$ to be 338.9 $\pm$ 4 kcal/mol. Within a particular structural type of boron hydrides, it is generally believed that the acidity increases with molecular size. Thus, for the *nido* boron hydrides, we would expect B$_5$H$_9$ to be more acidic that B$_2$H$_6$. Although the gas phase acidities of these compounds were to our knowledge unknown until our measurements, the general trend holds for the members of the series studied thus far. Consistent with the stuctural information on B$_5$H$_8^-$ is our observation that three H's exchange with DOAc. This, however, is the only notable chemistry observed. Other reactants, ones that readily react with B$_2$H$_3^-$, for example, are unreactive with B$_5$H$_8^-$

The B$_4$H$_5^-$ Anion: Preliminary studies of this anion with carboxylic acids are very interesting:

$$B_4H_5^- \quad + \quad CH_3CO_2H \quad \rightarrow \quad B_4H_7O^- \quad + \quad CH_2=C=O \quad (11)$$

The structure of B$_4$H$_5^-$ is unknown and speculation about reaction 11 must await further computational study. Nevertheless, it is clear that tis reaction involves dehydration. When DOAc replaces HOAc, the boron-containing product has incorporated deuterium.

The B$_{10}$H$_{14}^-$ Anion: To this point, our major interest in this anion has resulted from its CID behavior (eq. 6). The large number of CID products, particularly those with high boron-to-hydrogen ratios, suggest a number of interesting studies; however, the natural abundance problem referred to earlier is particularly severe in such large clusters. As a result, it is very difficult to mass select ^{10}B$_{10}$H$_{14}^-$, since the ^{10}B abundance is only 19%. Obviously, the amount of naturally abundant ^{10}B$_{10}$H$_{14}^-$ is vanishingly small. It is also impractical to mass select ^{11}B$_{10}$H$_{14}^-$ because, with clusters as large as ten boron atoms, there is then ambiguity concerning the number of boron atoms. An important rationale for preparing labelled diborane is to be able to produce large quantites of labelled B$_{10}$H$_{14}^-$ so that we can mass select reasonable quantities of its CID products.

The Carborane Anions: We have investigated several carborane compounds. Two of these, the diethyl and dimethyl derivatives, undergo proton abstraction with HO$^-$ to give their respective M-1 anions with the structure shown:

R
R B—H
H—B B—H
B H
H
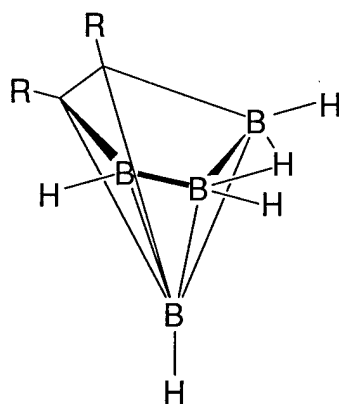
A value of ΔG^{o}_{acid} for the parent diethyl-carborane has been determined and is 331.7± 5 kcal/mol, indicating that it the parent carborane is a stronger gas phase acid than HCl (ΔG^{o}_{acid} = 340 kcal/mol). The diethyl anion undergoes two H-D exchanges with DOAc, although its likely structure (that shown) has only one bridging H. The CID behavior of both the diethyl and dimethyl anion are quite interesting, since both undergo a series of m/z = 14 losses. These processes are complicated. We have also studied ortho-carborane (1,2-dicarbadodecaborane), $H_2C_2B_{10}H_{10}$. In this compound the *closo* dodecaborane structure has two adjacent vertex BH's replaced by CH's (thus, its common name of ortho). Preliminary studies of this stable carborane, having natural abundance boron, were frought with the kind of difficulties mentioned earlier. However, we have been successful in obtaining this compound labeled with greater than 95%[10]B. A crude ΔG^{o}_{acid} of the parent ortho-carborane has been determined to be 337 ± 9 kcal/mol, which is similar to the diethyl-carborane just discussed. Its M-H anion can be obtained by proton abstraction with HO⁻ in the source region and can be cleanly mass selected. The anion obtained is remarkably stable and shows only small amounts of dissociation under CID conditions (only losses of H_2 and BH_3 have been observed). The anion undergoes one H-D exchange with methanol-OD, but otherwise is quite unreactive.

Ab Initio Computational Studies on Anions: Our intial work using *ab initio* computational methods has been on small boron hydride anions, particularly ones we have been able to study or observe as products of various reactions. Both B_2H_3⁻ and its common product, B_2H_3O⁻, which generally forms in its reaction with oxygen-containing neutrals, have been studied. In addition, a series of B_3H_n⁻ species have been considered, since (1) the anions where n = 2, 4, and 6 have been observed in CID studies and (2) these anions offer a huge number of structual possibilities. We felt it was particularly important that a number of different structural possibilities be considered, since anions of these types are virtually unexplored. Our studies have determined the energies of geometry optimized structures of various minima on the potential energy surface of a particular anion. We have not yet undertaken studies of actual reactions,

although we plan to do so in collaboration with Professor Mark S. Gordon of Iowa State University (*vide infra*).

Summary computational results for $B_2H_3{}^-$ have been tabulated in a previos report. The singly H-bridged structure is about 5 kcal/mol more stable
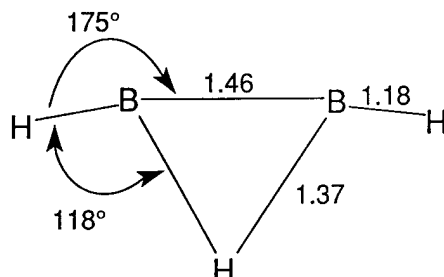

than H_2BBH^-. While this result has guided our thinking in considering the reactivity of this anion (*vide supra*), it is clear that we need to examine the details of reaction pathways to fully understand its reactivity. The structural features of H_2BBH^- are given below:
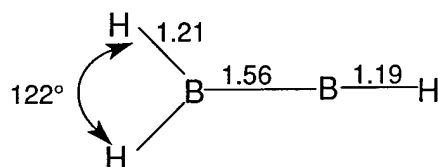

Both of these structures are planar and have terminal B-H bond distances of about 1.20 Å. The terminal hydrogens of the bridged structure are, surprisingly to us, bent toward the bridging H. The bridging B-H and B-B distances are about 1.37 and 1.46 Å. We have found in a number of other computations that the terminal B-H distance is always about 1.2 Å, but that B-B and bridging B-H distances vary considerably.

The anion $B_2H_3O^-$ has been optimized at the HF/6-31++G(d,p) level to give a H_3B-B-O^- structure, which is more than 500 kcal/mol more stable than the next higher energy structure that has an oxygen bridge, $H_2B(O)BH^-$. Interestingly, the most stable computed structure is isoelectronic with the known stable borane adduct $H_3B:CO$.

The $B_3H_2{}^-$ computational studies have been previously tabulated. The planar cyclic structure shown
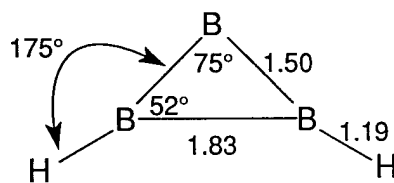
is about 17 kcal/mol more stable than linear HBBBH

$$H \text{———} B \text{———} B \xrightarrow{1.50} B \xrightarrow{1.18} H$$
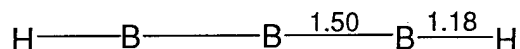
and far more stable than the other structures. This lowest energy cyclic anion has an unexpected structure. Its B-H bond distances are normal, but the different B-B distances are surprising. Thus, the B-B distance between two BH borons is 1.83 Å while that between a BH and an unsubstituted B is only 1.50 Å. These structural features are reflected in the B-B(H)-B(H) internal bond angle of 52 ° and the B(H)-B-B(H) angle of 75 °. The linear anion has a B-B distance of 1.50 Å.

A summary of the computations on the $B_3H_4{}^-$ species was reported earlier. The most stable $B_3H_4{}^-$ species is the planar cyclic structure shown:
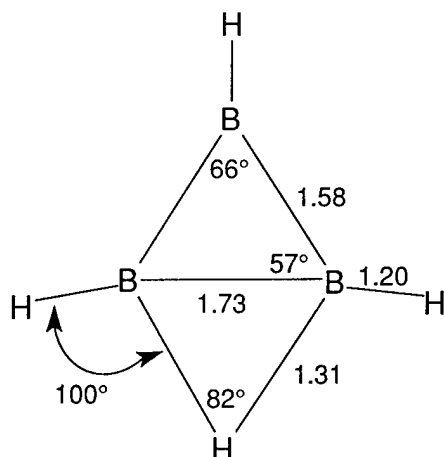
Only about 5 kcal/mol less stable is the following structure:
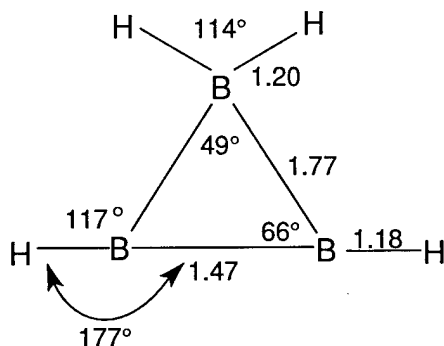
An examination of the features of the most stable $B_3H_4{}^-$ species shows some interesting similarities to the most stable $B_2H_3{}^-$ species. Examining the bridged portion of these two structures, we see not only some quite similar bond distances, but the terminal B-H's angled toward the bridging H. In the $B_3H_4{}^-$ species, these H's are bent closer to the bridging H, which may result from some

repulsive interactions with the upper BH. The upper BH affects the lower B-B bond distance as well, since in the $B_3H_4^-$ species it is somewhat shorter than in $B_3H_2^-$.

Ab initio studies of the $B_3H_6^-$ species have only recently begun. There are a great many structural possibilities to examine and we expect this to require some time. Schleyer and coworkers have recently examined the $B_3H_8^-$ anion by computational methods. They determined that the following C_{2v} structure
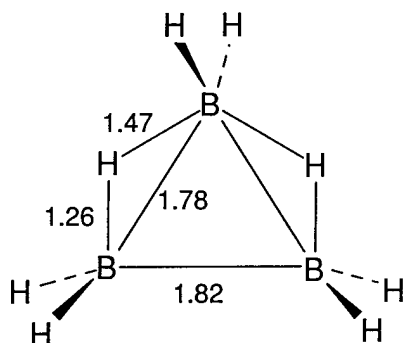
has the lowest energy of the two considered.

Brief Comments on Reactivity Studies of Anions: We have studied not only the anions briefly discussed above, but a variety of others as well. Certain trends have been observed, but the overwhelming impression such anions give is one of extremely attenuated reactivity. Thus, for example, our expectation that the very stable ortho-carborane anion would have little reactivity has been met, but our expectaion that those anions with high boron-to-hydrogen ratios would all be highly reactive has not. While $B_2H_3^-$ does show a remarkable and varied reactivity, it is not all that reactive, and other anions like $B_4H_3^-$ and $B_4H_5^-$ are not nearly as reactive. These results suggested that we consider an entirely different approach to these systems. As a result, we initiated studies on positive boron-containing ions which were proceeding nicely when funding for the third year of this project was not forthcoming. These studies are briefly described below.

Cation Studies of Boron: The unique characteristics of our FA-SIFT have allowed us to mass select various boron-containing cations and study their quite remarkable reactivity. A prime example has been BH_2^+, which we have examined in some detail. Its reactivity contrasts with that of CH_3^+ markedly (Table 1 summarizes the reactivity of BH_2^+, B^+, and CH_3^+). BH_2^+ reacts specifically with D_2 to give BHD^+ and HD with only a small amount (9%) of double H-D scrambling. In contrast, CH_3^+ gives four times greater H-D scrambling. The potential energy surface of these reactions have been explored by ab initio methods [MP4/6-311G**//MP2(full)/6-311G**] in collaboration with C. H. Depuy. Interaction of BH_2^+ and D_2 leads to a stable structure (A) some 15

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A   B   C
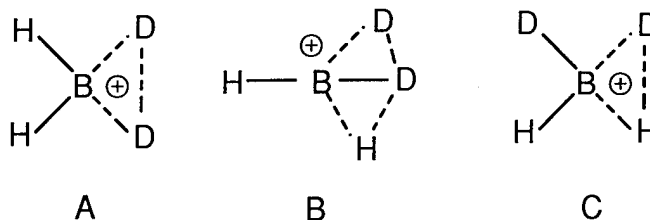
kcal/mol lower in energy than the reactants. This then is transformed through transition state B (about 2 kcal/mol above the entrance channel) to an equivalent "scrambled" structure C from which products form.

In a similar way, BH_2^+ has been shown to react with the methane to give specific reactions, which contrast with the behavior of CH_3^+. Thus, BH_2^+ reacts with CH_4 to produce CH_3BH^+ and dihydrogen. Reaction with methane gives incomplete scrambling while that in the reaction of CH_3^+ and CH_4 is markedly different. Again in collaboration with C. H. Depuy, *ab initio* computions have helped to characterize the reaction potential surface, in this case of the reaction of BH_2^+ and methane. These two interact initially to produce a species that is some 35 kcal/mol more stable than the reactants. This species is a doubly H-bridged cation D. The bond between carbon and boron is

D   E
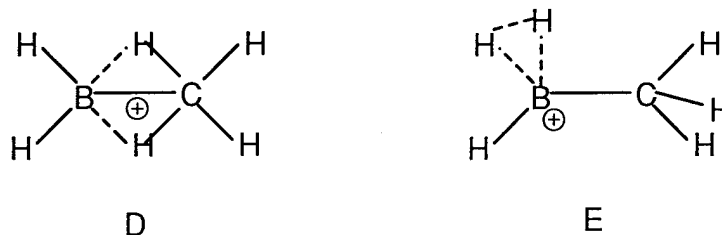
short and we tend write a bond there as well as the two bridges. This minimum energy species connects to other higher energy species that make clear how the products form. Thus, a tranistion state (E) about 25 kcal/mol higher in energy has the structure shown above. It is easy to see that the H_2 portion is indeed two hydrogens that are closely situated before their loss as dihydrogen. A number of other species on this surface as well as the far more complicated surface of BH_2^+ and ethane begin to give a good picture of the details of such reactions.

A number of other reactions of BH_2^+ and CH_3^+ have been studied and are given summarized in Table 1. BH_2^+ undergoes reaction with other simple hydrocarbons as expected; in additon, it has quite complex chemistry with unsaturated compounds like ethylene, allene, acetylene, and benzene. Reactions with a number of other neutral reactants have been studied as well (Table 1). Other simple boron cations have been investigated in a preliminary way such as B^+, $B_2H_5^{+,}$, and $B_2H_2^+$.

Computational Studies on Titanium and Silicon Hydrides: When we realized that FA-SIFT experiments on Ti and Zr ions were not practical because of the extreme lack of volatility of their precursor species, we decided that a computational approach might provide some interesting insights into various species. Fruitful previous collaborations with Professor Mark Gordon suggested that we might join forces again. A subcontractural arrangement

allowed us to partially support Dr. Takako Kudo to pursue work on titanium that had begun in Gordon's group. Thus, electron structure calculations on several TiH_3X species with triple zeta polarization basis sets with second perturbation effects considered allowed molecular and electronic structures to be determined. These Group 4 species can be compared to analogous species for silicon in Group 14. In preliminary work, it was found that second period X groups like CH_3, NH_2, and OH had similar structures to anlaogous silicon compounds. However, when X= SiH_3, PH_2, and SH, much more interesting bridged structures were obtained. Work has continued (and is continuing) on the mechanism of thermal decompostiton of H_3TiOH and a series of related cyclic species of silicon.

Table 1

Reactivity Comparisons of BH_2^+, B^+, and CH_3^+

	H$_2$	D$_2$
$^{12}CH_3^+$ (m/z=15)		$CH_2D^+ + HD$ (65%) $CHD_2^+ + H_2$ (35%) $k_r= 6.8 \times 10^{-10}$
$^{12}CD_3^+$ (m/z=18)	$CHD_2^+ + HD$ (80%) $CH_2D^+ + D_2$ (20%) $k_r=5.2 \times 10^{-10}$	
$^{10}B^+$ (m/z=10)	NR	
$^{11}BH_2^+$ (m/z=13)		$BHD^+ + HD$ (91%) $BD_2^+ + H_2$ (9%) $k_r=4.05 \times 10^{-11}$ $k_L=1.142 \times 10^{-9}$ (eff=3.4%)
$^{11}BD_2^+$ (m/z=15)	$BHD^+ + HD$ (93%) $BH_2^+ + D_2$ (7%) $k_r=3.75 \times 10^{-11}$ $k_L=1.58 \times 10^{-9}$ (eff=2.4%)	

	CH4	CH3CH3	CH3CH2CH3
$^{12}CH_3^+$ (m/z=15)	Adduct - H_2 k_r=1.1x10^{-9}	$C_2H_3^+$ + CH_4 (85%) $C_3H_5^+$ + H_2 + H_2 (9%) $C_3H_7^+$ + H_2 (6%)	
$^{13}CH_3^+$ (m/z=16)		Adduct - $^{13}CH_4$ (78 %) Adduct - $^{12}CH_4$ (9 %) Adduct - H_2 (13 %)	
$^{12}CD_3^+$ (m/z=18)	Adduct - H_2, HD, D_2	Adduct - CD_3H Adduct - H_2, HD, D_2 (vs)	
$^{10}B^+$ (m/z=10)	NR	Adduct - H_2 (38) Adduct - H (39) Adduct (40) (other small peaks)	[HBCH$_3$]$^+$ + CH_2CH_2 Adduct - BH_3 Adduct - H_2
$^{11}BH_2^+$ (m/z=13)	Adduct - H_2 [HBCH$_3$]$^+$ k_r=1.1x10^{-9} k_L=1.4x10^{-9} (Eff=75.6)	Adduct - H_2 (41) Adduct - CH_4 [HBCH$_3$]$^+$ (27)	isopropyl cation (43) + BH_3 Adduct - H_2 ethyl cation (29) + BH_2CH_3 [HBCH$_3$]$^+$ + CH_3CH_3
$^{11}BD_2^+$ (m/z=15)	Adduct - HD [DBCH$_3$]$^+$	Adduct - HD (42) Adduct - CH_4 [DBCH$_2$D]$^+$ (29)	isopropyl cation (43) + BD_2H Adduct - HD ethyl cation (29) + BD_2CH_3 [DBCH$_3$]$^+$ + CH_3CH_2D [HBCH$_3$]$^+$ + CH_3CHD_2

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	CH2=CH2	CH2=C=CH2	HC≡CH
$^{12}CH_3^+$ (m/z=15)	vinyl cation (27) + CH_4 $[CH_2=CH-CH_2]^+$ (41) + H_2 ethyl cation (29)	Adduct - H_2 prot trans (41); hydride trans(39) ethyl cat (29); vinyl cat (27)	cyclopropenium cation (39) + H_2
$^{13}CH_3^+$ (m/z=16)	vinyl cation (27 : 28) = 2:3 (implies scrambling in 3-membered intermediate) A - H_2 (42); ethyl cat (29)	Adduct - H_2 prot trans (41); hydride trans(39) ethyl cat (29:30) equal amounts; vinyl cat (27:28) equal amounts	
$^{12}CD_3^+$ (m/z=18)	scrambling in all products	Adduct - H_2, HD, D_2 H/D mixing on other products	H/D mixing: $[C_3H_2D]^+$ + D_2 $[C_3HD_2]^+$ + HD $[C_3D_3]^+$ + H_2
$^{10}B^+$ (m/z=10)	$[H-B-C≡C-H]^+$ (36) + H_2 $^{10}BH_2^+$ + C_2H_2 Adduct		Adduct (36)
$^{11}BH_2^+$ (m/z=13)	Adduct - H_2 (39) Adduct (41)		Adduct - H_2 $[H-B-C≡C-H]^+$ (37)
$^{11}BD_2^+$ (m/z=15)	Adduct - H_2, HD (equal amounts) Adduct (43)		Adduct - HD $[D-B-C≡C-H]^+$ (38)

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	Benzene	Benzene - D$_6$
$^{10}B^+$ (m/z=10)	Add - H$_2$ (86) Add - C$_2$H$_2$ (62) Add - H$_2$ - C$_2$H$_2$ (60) ?	
$^{11}BH_2^+$ (m/z=13)	Adduct (91) Adduct - H$_2$ (89)	Adduct (97) Adduct - H$_2$ (95) Adduct - HD (94) Adduct - D$_2$ (93)

	Toluene	Toluene - CD$_3$	Toluene - D$_8$
^{10}B$^+$ (m/z=10)	Add - C$_2$H$_2$ (76) Adduct - H$_2$ (100) Adduct (102) ?	Add - C$_2$D$_2$ (77) Add - C$_2$HD (78) Add - C$_2$H$_2$ (79) Adduct (105) Adduct + H$^+$ (106)	
^{11}BH$_2^+$ (m/z=13)	Adduct (105) Adduct - H$_2$ (103) Benzyl Cation (91) Add - C$_2$H$_4$ (77)	Adduct (108) Adduct - H$_2$ (106) Adduct - HD (105) Benzyl$^+$ d-2 (93) loss of C$_2$H$_2$, C$_2$HD, and C$_2$D$_2$ from 105, 106. (80,79,78,77:)	Adduct (113) Adduct - HD (110) Adduct - D$_2$ (109) Adduct - D$_2$ - C$_2$D$_2$ (81) Adduct - HD - C$_2$D$_2$ (82) Adduct -H$_2$, - C$_2$D$_2$ (83)

	SiH$_4$ (32)	B$_2$H$_6$ (28)
^{12}CH$_3{}^+$ (m/z=15)	SiH$_3{}^+$ + CH$_4$ (94%) CH$_3$Si$^+$ + H$_2$ + H$_2$ (3%) CH$_3$SiH$_2{}^+$ + H$_2$ (3%)	B$_2$H$_5{}^+$ (27) + CH$_4$ or [HBCH$_3$]$^+$ (27)+ H$_2$ + BH$_3$ (also 26 & 25)
^{10}B$^+$ (m/z=10)	SiH$^+$ (29) + BH$_3$ Adduct - H$_2$ (40)	Adduct - H$_2$ (36) B$_2$H$_5{}^+$ (27)+ ^{10}BH ^{10}B^{11}BH$_3$ (24) + ^{11}BH$_3$
^{11}BH$_2{}^+$ (m/z=13)	Adduct - H$_2$ (43) SiH$_3{}^+$ (31) + BH$_3$	
^{11}BD$_2{}^+$ (m/z=15)	Adduct - H$_2$, HD, D$_2$ Adduct - BH$_3$, BH$_2$D, BHD$_2$	

	CO	CO$_2$	COS
^{12}CH$_3^+$ (m/z=15)	NR	NR	CH$_2$SH$^+$ + CO
^{10}B$^+$ (m/z=10)	NR	Adduct (54)	Adduct (70)
^{11}BH$_2^+$ (m/z=13)	BH$_2$O$^+$ (29)+ C (high flow) Adduct (41)	BH$_2$O$^+$ (29)+ CO CO$^+$ (28)+ BH$_2$O	BH$_2$S$^+$ (45) + CO

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	CS$_2$	H$_2$S	CDCl$_3$ (119)
^{12}CH$_3^+$ (m/z=15)	NR	CH$_2$SH$^+$ + H$_2$	
^{12}CD$_3^+$ (m/z=18)		Add - H$_2$, HD, D$_2$	
^{10}B$^+$ (m/z=10)	Adduct (86)		CDCl$_2^+$ (84)+ BCl
^{11}BH$_2^+$ (m/z=13)	Adduct - CS (BH$_2$S$^+$) (86)		CDCl$_2^+$ (84)+ B H$_2$Cl

	H_2O (18)	D_2O	NH_3
$^{12}CH_3^+$ (m/z=15)	Adduct $[CH_3OH_2]^+$ (33) $[CH_2OH]^+$ + H_2 (31) H_3O^+ (19)		NH_4^+ Adduct - H_2 Adduct
$^{12}CD_3^+$ (m/z=18)	Adduct $[CD_3OH_2]^+$ (36) Adduct $[CD_3OHD]^+$ (37) Adduct $[CD_3OD_2]^+$ (38) Adduct - HD, D_2		NH_3D^+ Adduct - HD Adduct
$^{10}B^+$ (m/z=10)	Adduct - H· (27) H_3O^+ (19) $B(OH)_2^+$ (44)	Adduct - D· (28) Adduct (30)	Adduct - H (26) Adduct (27)
$^{11}BH_2^+$ (m/z=13)	Adduct - H_2 (29) H_3O^+ (19) + BH	Adduct - HD· (30) Adduct - D_2 (29)	
$^{11}BD_2^+$ (m/z=15)	Adduct - HD (30)		

	CH_3OH	CH_3OD	CH_3CH_2OH
$^{10}B^+$ (m/z=10)	Adduct - H· (41) CH_3^+ + BOH BOH^+ (27) + CH_3 $CH_3OH_2^+$ (33)	Adduct - D· (41) CH_3^+ + BOD BOD^+ (28) + CH_3 CH_3OHD^+ (34)	$CH_3CH_2^+$ + BOH $CH_3CH_2OH_2^+$ (47)
$^{11}BH_2^+$ (m/z=13)	BH_2O^+ (29) + CH_4 $CH_3OH_2^+$ (33) + BH Add - H_2 (43) CH_3^+ (15)+ BH_2OH	$HBOH^+$ (29) + CH_3D $HBOD^+$ (30) + CH_4 $CH_3OH_2^+$ (33) + BD CH_3OHD^+ (34) + BH Add - HD	BH_2O^+ (29) + CH_3CH_3 $CH_3CH_2OH_2^+$ (47) + BH

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